Stresses Generated by Anodic and Cathodic Polarization of a Titanium Thin Tilm Electrode

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Stress changes during anodic and cathodic polarization of titanium thin film electrode on a glass substrate in pH 8.4 borate solution were measured by a laser beam bending method, based on Stoney's work[1] modified later by Láng and Seo[2]. The titanium film of 0.25μm was formed on a thin glass plate by a magnetron sputtering method.

Figure 1 shows the changes in current density(a) and deflection(b) for the potential scanning from 5.7 to –0.5V(RHE) obtained after applying anodic potential of 5.7V(RHE) to the titanium thin film/glass electrode system for 1h. As soon as the potential applied, it produced an instantaneous compressive movement. Based on the modified Stoney equation[2] and the assumption that the applied current was used only for oxide formation, the surface stresses of the oxide film formed at 5.7V(RHE) for 1h before the potential scanning were calculated to be about 3 GPa. The compressive stresses due to the oxide formation were also found in the work of Ueno et.al[3] and well understood by considering the molar volume difference between $V_{ox(anatase)}$ (= 20.8 cm^3mol^{-1}) or $V_{ox(rutile)}$(=18.8cm^3mol^{-1}) and V_{Ti} (= 10.6 cm^3mol^{-1}). As the potential moved from 5.7 to around 4.5 V(RHE), the current showed typical passivation current and the deflection moved with tensile direction. As the potential was passed through 4.5 to 0.5 V(RHE), the current showed a steady state and the deflection moved with tensile direction. A current peak was observed in the potentials from 0.5 to –0.2 V(RHE). However, the deflection moved still with tensile direction from 0.5 to 0.0V(RHE) and the deflection plateau was found between 0.0 and about –0.2 V(RHE). Considering that the flat band potential of Ti, $\phi_{FB,Ti}$, is about 0 V(RHE), the tensile movement is thought to be due to the removal of electrostrictive stress which becomes zero at the flat band potential. Below about -0.2V(RHE), we could find a noticeable increase in cathodic current and an abrupt deflection transition from tensile to compressive direction. According to Ohtsuka et.al[4], the composition change of the anodic oxide film, such as $TiO_2 + H^+_{aq} + xe = TiO_{2-x}(OH)_x$,due to hydrogen absorption into the film starts from –0.25V(RHE) and finally reaches TiOOH at –0.9V(RHE). Thus the compressive movement was thought to be produced by the volume expansion of the film due to the compositional change from TiO_2 to TiOOH resulting from the hydrogen absorption reaction.

Figure 2 shows the transients in current density(a) and deflection(b) produced by various potential steps of 5.7→ -0.5→0.5→-0.5→0.5→-0.5→5.7 V(RHE). After applying each potential step, the potential was held there for 1h to observe steady state behavior. At each potential step, we could observe the sudden increase/decrease of current and deflection followed by a decay to another steady-state value. It is noted that the charging current and deflection which were produced by the potential step down are increased with increasing the number of potential step down process.

References

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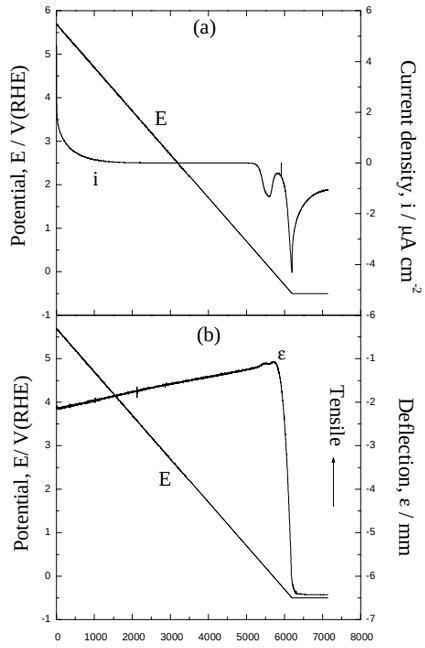

Figure 1. Changes in current density(a) and deflection(b) for the potential scanning from 5.7 to –0.5V(RHE) at 1mV s^{-1} obtained after applying anodic potential of 5.7V(RHE) to the titanium thin film/glass electrode system for 1h in pH8.4 borate buffer solution.

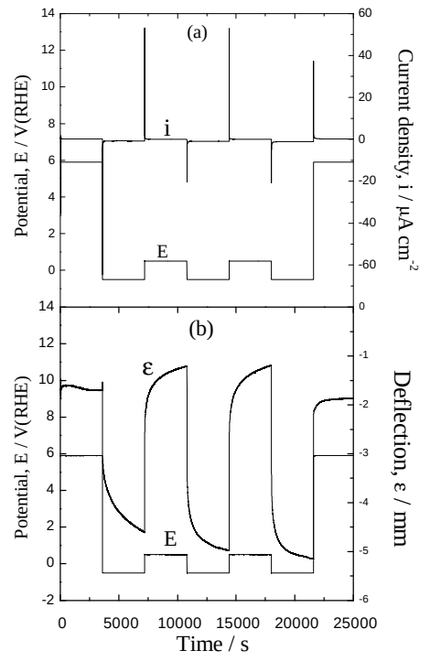

Figure 2. Changes in current density(a) and deflection(b) for the potential steps of 5.7→ -0.5→0.5→-0.5→0.5→-0.5→5.7V(RHE) to the titanium thin film/glass electrode system for 1h in pH8.4 borate buffer solution(The potential was held for 1h between each potential step).